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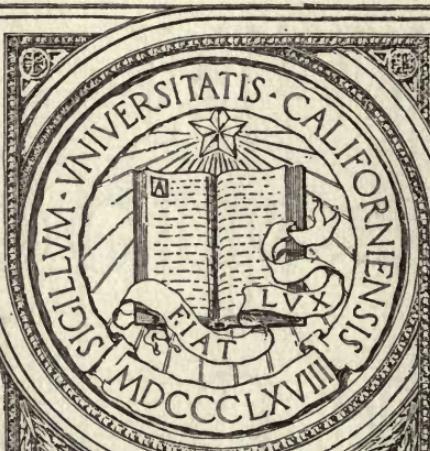
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I. TUNGSTEN HEXABROMIDE.

II. TUNGSTEN COMPLEXES.

A THESIS

PRESENTED TO THE FACULTY OF THE GRADUATE SCHOOL OF THE  
UNIVERSITY OF PENNSYLVANIA IN PARTIAL FULFILLMENT  
OF THE REQUIREMENTS FOR THE DEGREE OF  
DOCTOR OF PHILOSOPHY

BY

HARRY BECKERMAN

PHILADELPHIA, PA.

1918



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90 JULY  
1920

# I. TUNGSTEN HEXABROMIDE.

## INTRODUCTION.

In 1851, v. Borch<sup>1</sup> passed bromine over highly heated tungsten and obtained tungsten pentabromide. In 1857, Riché<sup>2</sup> employing the same reaction, obtained what he believed to be tungsten hexabromide, submitting, however, no analyses to support his belief. In 1861, Bloomstrand<sup>3</sup> repeated the work of Riché and showed that the conditions outlined by the latter yielded pentabromide and not hexabromide. In 1872, Roscoe<sup>4</sup>, in an endeavor to prepare tungsten hexabromide, acted upon metallic tungsten with bromine at a red heat, in an atmosphere of carbon dioxide, and obtained tungsten pentabromide. Tungsten hexabromide was first prepared in this laboratory, in 1896, by Schaffer and Smith,<sup>5</sup> by allowing bromine to act on tungsten metal at a gentle heat, in an atmosphere of nitrogen. These investigators attributed their success in the preparation, to the low temperatures at which they operated, the high temperatures, previously employed, tending to prevent the formation of hexabromide. They also replaced the carbon dioxide by nitrogen, fearing that the former would be deoxidized in the reaction with the formation of oxybromides. The amount of tungsten hexabromide obtained, however, was small and the two complete analyses of the product were not very concordant. As a consequence, a confirmation of this work seemed highly desirable. The purpose of the present investigation was to confirm the existence of tungsten hexabromide as well as to determine more exactly the conditions under which it is formed.

In 1916, Hill,<sup>6</sup> in this laboratory, noticed that the action of chlorine on tungsten metal to form tungsten hexachloride is

<sup>1</sup> Oefvers. af. k. Vetensk. Akad. Förh. 1851, 150.—Handbuch der anorganischen Chemie, 1912 (Gmelin-Kraut) 111, I, 762.

<sup>2</sup> Ann. Chim. Phys. (3) 50 (1857) 24.

<sup>3</sup> Jour. pr. ch. 82, 429.

<sup>4</sup> Ann. der. chem. 162, 362.

<sup>5</sup> Am. Ch. Jour. 18 (1896), 1098.

<sup>6</sup> Jour. Am. Chem. Soc. 38 (1916), 2383.

catalyzed to a remarkable degree by the presence of a small amount of platinum black. The temperature of formation of tungsten hexachloride was reduced and the speed of reaction was increased. The idea presented itself that this method applied to the preparation of tungsten hexabromide might so far facilitate its formation that a good yield of this body might be obtained.

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## EXPERIMENTAL PART.

### MATERIALS.

The best results were obtained with a finely divided tungsten, formed by heating tungsten trioxide in hydrogen for a long time, at as low a temperature as possible, care being taken that the metal was entirely reduced. The tungsten formed in this way is black in color and is more finely divided than the grey variety. The metal was not permitted to remain in contact with the air because it absorbs both oxygen and moisture. It was preserved in dry hydrogen.

The bromine used was prepared by treating ordinary bromine with potassium bromide and manganese dioxide, to remove chlorine and organic matter. This mixture was allowed to stand over night, and the bromine was then distilled out. It was washed three times with distilled water and then treated with fused  $\text{CaCl}_2$  over night and distilled again. The treatment with fused calcium chloride and the distillation were repeated twice. The distillation of the bromine took place entirely in glass. The bromine was preserved in well stoppered bottles in a desiccator over concentrated sulphuric acid.

Since platinum black absorbs oxygen from the air, it was mixed with the tungsten trioxide before the latter was reduced in hydrogen. The tungsten formed was thus intimately mixed with the platinum and was entirely free of oxygen.

### PROCEDURE.

The preparation of tungsten hexabromide is very difficult. Unless the greatest possible attention is paid to every minute detail, no hope for success can be entertained. The greatest

difficulty experienced was the elimination of small traces of oxygen which leaked into the apparatus, in spite of precautions taken to prevent it. This trace of oxygen was removed by placing in the tube A, before the boat E, a long layer of sugar carbon. This was heated to redness. The carbon dioxide formed, being diluted with a large quantity of nitrogen, passed on without entering the reaction. Sugar carbon made by heating pure cane sugar contains oxygenated organic bodies, even when the carbon is heated to redness in a blast lamp. These oxygenated organic bodies were removed by heating the carbon to a high temperature in bromine vapor until moisture and liquid brominated bodies were no longer given off. The sugar carbon was then heated in dry hydrogen and preserved in that gas.

The character of the tungsten used is vital to the success of the preparation. Black tungsten proved successful, the grey variety giving mostly tungsten pentabromide mixed with a little tungsten hexabromide.

The air was displaced from the apparatus by means of a stream of nitrogen which was made as follows. Air was forced by means of a water blast through potassium hydroxide solution, to remove carbon dioxide, then through two wash bottles containing concentrated ammonia water. The air took up ammonia gas and then passed into a long Jena tube containing red-hot copper. The hydrogen of the ammonia combined with the oxygen of the air to form water. The latter was condensed in an empty cooled flask. The nitrogen from the air and that from the ammonia passed into another Jena tube containing a red-hot, reduced copper spiral, to remove the last traces of oxygen. The gas was then washed through two bottles of dilute sulphuric acid to remove traces of ammonia which might still be retained by the nitrogen. The rest of the apparatus is as pictured in Fig. 1. Moist chromous acetate mixed with glass beads removed the last traces of oxygen. From here on, the apparatus was made entirely of glass, no rubber connections or stoppers being used.

The nitrogen was thoroughly dried by passage through boiled sulphuric acid, solid potassium hydroxide and phosphorus pentoxide. The gas then passed through the U-tubes, F and G, and then into the tube A. After the tube A was placed an empty

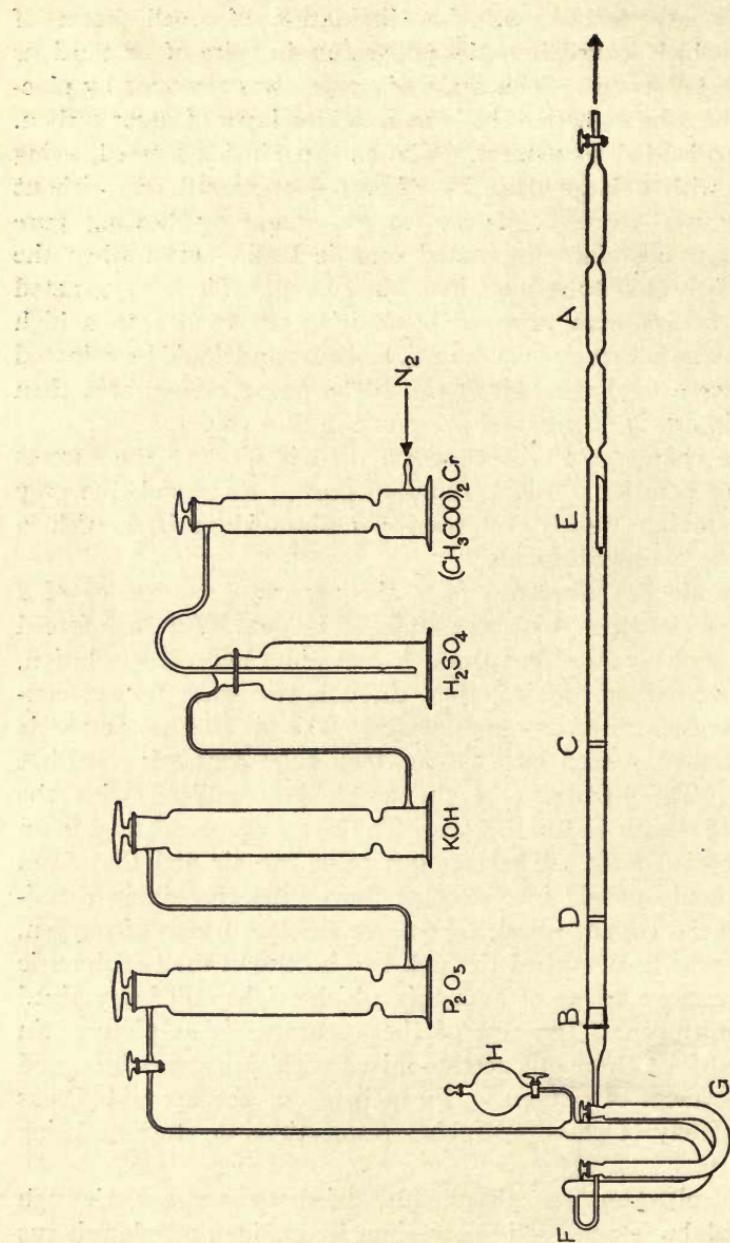


FIGURE 1

tower to condense the excess of bromine, a tower with fused  $\text{CaCl}_2$  and then a vessel containing soda lime to prevent the bromine vapor from reaching the air.

A porcelain boat containing the tungsten, mixed with a trace of platinum, was removed from the tube in which it was reduced in hydrogen. It was quickly inserted into the tube A through the ground-glass joint B. A plug of dried glass wool was inserted and then the tube was filled from C to D with sugar carbon. The ground glass connection B was shut and tightly clamped by means of rubber bands. It was coated with paraffine on the outside. The current of dry nitrogen was continued for eight hours more to remove the air and thoroughly dry the apparatus.

The sugar carbon was heated to redness. Bromine was then allowed to drop from the separatory funnel H into the U-tube F, from which it passed into G. G contained glass wool moistened with boiled sulphuric acid to remove traces of moisture which might be introduced by the bromine. F and G were immersed in a beaker of hot water. When an excess of bromine had reached the porcelain boat, E, the latter was gently heated. An excess of bromine was maintained at the moment of formation, otherwise tungsten pentabromide would have been formed. The latter does not combine with more bromine and stays as tungsten pentabromide. The temperature of the tube at E was ascertained by placing a thermometer in contact with it. The reaction started at  $200^\circ \text{ C}$ . At  $230^\circ \text{ C}$ . it was fairly rapid. The tungsten hexabromide rose from the boat in the form of a heavy reddish brown vapor which condensed in the colder part of the tube to a reddish brown liquid. The latter on cooling solidified with a crackling sound, forming a crystalline solid. The first portion was driven beyond the point at which it was intended to collect the main part of the preparation. The remainder was fractionally redistilled in an excess of bromine vapor. A non-volatile black residue was left behind. The middle fraction was collected between two constrictions. After cooling, the excess bromine was removed by means of the stream of nitrogen. The bulb containing the preparation was then sealed off.

Tungsten hexabromide is a blue-black crystalline solid which can, with care, be sublimed in bromine vapor in the form of blue-black shining needles. It appears to be soluble in liquid bromine. It fumes in the air. Water decomposes it giving a deep blue oxide. Ammonium hydroxide dissolves it completely. Concentrated sulphuric acid and concentrated nitric acid form tungstic oxide. On heating it evolves bromine.

### METHOD OF ANALYSIS.

#### TUNGSTEN CONTENT.

A porcelain crucible containing a weighed portion of the preparation was placed in a covered beaker containing a little warm water. The water vapor acted rapidly on the preparation, decomposing it, without causing it to spatter. The mass liquified. The crucible was then placed on a stove plate and the contents carefully evaporated to dryness. Dilute nitric acid was added and again evaporated to dryness. Moderately concentrated nitric acid was added; then finally concentrated nitric acid was added repeatedly, evaporating to dryness each time. The tungsten trioxide so formed was ignited and weighed.

#### BROMINE CONTENT.

A weighed sample was placed in a Bunsen apparatus. Nitric acid was added by means of a separatory funnel fused into the delivery tube of the flask. The mixture was distilled into silver nitrate solution. The distillate, containing silver bromide, silver bromate and excess of silver nitrate, was transferred to a porcelain dish and evaporated to dryness. The residue was ignited to change the silver bromate to silver bromide. The dish was allowed to cool. Nitric acid was added and then hot distilled water containing a little nitric acid. The silver bromide was filtered and washed. It was weighed as silver bromide. The results are given in Table I.

TABLE I.

## Preparation No. 9.

Wt. of Sample.	Wt. of $\text{WO}_3$ .	% W.	% Br.	Theoretical Percentages.	
				WBr.	WBr.
0.1023 gr.	0.0366 gr. $\text{WO}_3$	28.35 W		31.52 W	27.72 W
0.4126 "	0.1492 " "	28.67 "		68.48 Br	72.28 Br
0.2156 "	0.0774 " "	28.43 "			
0.4249 "	0.1528 " "	28.53 "			
0.5236 "	0.8834 " AgBr		71.79 Br		

## Preparation No. 12.

Wt. of Sample.	Wt. of $\text{WO}_3$ .	% W.	% Br.
0.1575 gr.	0.0554 gr. $\text{WO}_3$	27.87	
0.8152 "	0.2882 " "	28.04	
0.0698 "	0.0243 " "	27.65	
0.6354 "	{ 0.2243 " " 1.0735 " AgBr	28.00	71.89
0.4582 "	{ 0.1623 " $\text{WO}_3$ 0.7730 " AgBr	28.09	71.80

THE ACTION OF CHLORINE AND BROMINE ON  
MOLYBDENUM MIXED WITH PLATINUM BLACK.

The success attained with the preparation of tungsten hexabromide raised the hope that platinum black would catalyze the reaction between chlorine and molybdenum. Chlorine acts on molybdenum metal at a dull red heat to form molybdenum pentachloride. It was thought that the temperature of formation would be reduced so that molybdenum hexachloride might be formed. The latter has never been obtained.

Finely divided molybdenum was mixed with platinum black and was subjected to the action of chlorine in an atmosphere of nitrogen. The action started at 40° C. Unless the chlorine was diluted with a large quantity of nitrogen, the reaction became so violent that the metal caught fire in the chlorine. The action was allowed to proceed slowly at 50° to 60° C. Large, black, highly lustrous crystals formed in the boat. These were slowly sublimed out, collected between two constrictions and sealed up in glass. They were analyzed by the method described under

tungsten hexabromide. Care was taken to prevent volatilization of the molybdenum trioxide, by careful ignition. The results are given in Table II.

TABLE II.

Wt. of Sample.	Wt. of $\text{MoO}_3$ .	% Mo.	% Cl.	Theoretical Percentages.	
				MoCl <sub>5</sub>	MoCl <sub>4</sub>
0.2065 gr.	0.1083 gr.	34.96		35.13 Mo	31.09 Mo
0.1843 "	0.0976 "	35.33		64.87 Cl	68.91 Cl
0.5168 "	0.2734 "	35.26			
0.1519 "	0.0799 "	35.02			
0.7313 "	{ 0.3875 "      35.32 1.9445 " AgCl		65.75		
		Average Mo 35.18			

The compound, therefore, was molybdenum pentachloride.

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Molybdenum pentabromide has never been made. Indeed, molybdenum tetrabromide is difficult to prepare, it being formed in small traces when bromine is passed over molybdenum, the chief product being molybdenum tribromide. Attention was next directed to the preparation of molybdenum pentabromide.

Molybdenum metal, mixed with platinum black, was heated in Br vapor. At 130° to 140° C., the reaction proceeded rapidly. Long, sharp, hairy needles formed above the boat. On resubliming they decomposed into yellow  $\text{Mo Br}_2$ . Therefore the boat was removed from the tube, the crystals were quickly detached and dropped into a weighing bottle. The substance was very voluminous, a large bulk of the hairy crystals weighing very little.

TABLE III.

Wt. of Sample.	Wt. of $\text{MoO}_3$ .	% Mo.	Theoretical Percentages.	
			MoBr <sub>4</sub>	MoBr <sub>3</sub>
0.0431 gr.	0.0155 gr.	23.89	23.08 Mo	19.36 Mo

The substance, therefore, was  $\text{MoBr}_4$ .

## II. TUNGSTEN COMPLEXES.

### INTRODUCTION.

Inorganic complexes play a more important rôle than is generally believed to be the case. The difficulty which is frequently met with, in the purification of substances can, often, be directly attributed to the formation of complexes. For example, Smith and Exner<sup>1</sup> in an exhaustive paper on the atomic weight of tungsten show conclusively that the difficulty of preparing pure tungstic acid is due to the ease with which the latter substance forms complexes. They found that on digesting tungstic acid, which was free of iron, with hydrochloric acid or nitric acid, in which iron was present, the latter would enter the tungstic acid. Iron, manganese, phosphorus and vanadium were extremely difficult to remove. Indeed an ammonium salt of a complex, containing the oxides of the above elements, was isolated. Similarly, the slimy, greenish or bluish white residue remaining when tungstic acid dissolved in ammonium hydroxide, was found by them to contain ammonium chloride. It was probably an ammonium chlorinated tungstic acid derivative.

Again, Rogers and Smith<sup>2</sup> have shown that the introduction of only a few tenths of one per cent of various dioxides, like  $TiO_2$  and  $ZrO_2$ , into ammonium vanadico-phospho-tungstate changed its properties and reactions entirely. The authors point out that in mineral analysis the influence of such minute amounts of supposedly foreign constituents is too often disregarded and not considered in the deduction of formulas.

As a consequence an intimate knowledge of complexes, the conditions under which they are formed, their analyses, are subjects of importance. The purpose of the present investigation is to continue the study of complexes which has been carried on in this laboratory for a number of years.

In 1895, Wolcott Gibbs,<sup>3</sup> the pioneer in this field of research,

<sup>1</sup> Proc. Am. Phil. Soc. 43 (1904), 123.

<sup>2</sup> Jour. Am. Chem. Soc. 25 (1903), 1223.

<sup>3</sup> Am. Chem. Jour. 17 (1895), 173.

prepared complexes containing molybdenum dioxide by boiling hydrated  $\text{MoO}_2$  with sodium para tungstate. From the deep orange colored solution, potassium bromide gave a buff colored precipitate which was recrystallized from water in small pale brown scales. Gibbs ascribed the formula  $5 \text{K}_2\text{O} \cdot \text{MoO}_2 \cdot 12 \text{WO}_3 \cdot 16 \text{H}_2\text{O}$  to the compound. It was thought that corresponding complexes containing tungsten dioxide might exist.

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### EXPERIMENTAL.

The reduction of hydrated, precipitated tungsten trioxide to hydrated tungsten dioxide by zinc and hydrochloric acid was found to be a difficult task. After five days' action, the reduction had not reached the tungsten dioxide stage. Several known methods were tried and the best was found to be the following: A large excess of tungsten trioxide was boiled up with sodium hydroxide solution. A small test portion of the solution was treated from time to time with dilute hydrochloric acid until a precipitate of tungstic acid no longer formed. This indicated the formation of a meta tungstate,  $\text{Na}_2\text{O} \cdot 4 \text{WO}_3$ . The solution was filtered. Zinc dust, added to this solution, turned it intense indigo blue. Dilute hydrochloric acid was then added. In a few minutes copper-red, hydrated tungsten dioxide formed. The increased speed of the reduction was due to the fact that the action took place in solution instead of in the solid phase. The tungsten dioxide was filtered and washed on the suction pump in an atmosphere of hydrogen.

I. Ammonium para tungstate, dissolved in water, was boiled up with the hydrated tungsten dioxide. A deep blue solution formed. The excess tungsten dioxide was filtered out carefully. On standing the solution turned bright green and then deep orange colored. The same changes in color took place in an atmosphere of hydrogen, so that the change was not due to oxidation. On heating, the orange colored solution changed back to green and then to deep blue. Potassium iodide, added in large excess, gave a buff colored precipitate. This was filtered out. It was soluble in hot water, difficultly soluble in cold.

It was recrystallized from water, coming down in beautiful light brown crystals. Sodium bromide, added to the orange colored solution, gave the light brown sodium salt. The similarity to the  $\text{MoO}_2$  compounds obtained by Gibbs is marked. Lead acetate gave a heavy yellowish white crystalline precipitate. Silver nitrate gave a red precipitate, somewhat soluble in hot water giving a red solution. Mercurous nitrate gave a reddish brown precipitate. Alcohol threw down the brown alkali salt. Manganous sulphate gave a white precipitate. The cobalt salt was rose colored, while a copper compound, precipitated by copper sulphate, was greenish yellow. Ferric chloride gave no precipitate. The barium salt was white.

#### ANALYSIS OF THE POTASSIUM SALT.

##### $\text{WO}_2$ CONTENT.

A weighed portion was dissolved in water. Dilute sulphuric acid was added and then an excess of standard potassium permanganate solution. The solution was warmed on the water bath. It was then cooled and an excess of ferrous ammonium sulphate, dissolved in water, was added. The excess ferrous iron was titrated back with potassium permanganate solution. The tungsten dioxide content was calculated.

##### $\text{WO}_3$ AND $\text{K}_2\text{O}$ CONTENT.

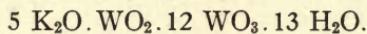
The complex was found to be only slowly decomposed by concentrated nitric acid or aqua regia. The following method proved satisfactory. A weighed sample was dissolved in hot water. A few cubic centimeters of dilute sulphuric acid and a little nitric acid were added. The solution was evaporated, in an air bath, to strong fumes. After cooling, water was added and the evaporation to fumes repeated. Nitric acid and water were added and the mixture was digested for one hour. The tungsten trioxide was filtered out and washed with hot water containing nitric acid. It was then ignited and weighed. The filtrate from the  $\text{WO}_3$  was evaporated to small bulk, transferred to a weighed crucible. The evaporation was continued, the sulphuric acid was driven off. The potassium sulphate was ignited

and weighed. The water was obtained by difference. The results are contained in Table 4.

TABLE IV.

Wt. of Complex.	Wt. of Constituent Found.	%	Theoretical % calculated for 5 K <sub>2</sub> O.WO <sub>2</sub> .12 WO <sub>3</sub> .13 H <sub>2</sub> O.
0.3072 gm.	0.0184 gr. WO <sub>2</sub>	5.99 WO <sub>2</sub>	5.83 WO <sub>2</sub>
0.4664 "	0.0271 " "	5.81 "	
0.3282 "	0.2465 " WO <sub>3</sub>	75.11 WO <sub>3</sub>	75.16 WO <sub>3</sub>
0.3236 "	0.2417 " "	74.69 "	
0.3282 "	0.0762 " K <sub>2</sub> SO <sub>4</sub>	12.55 K <sub>2</sub> O	12.69 K <sub>2</sub> O
0.3236 "	0.0768 " "	12.82 "	
	by difference	6.52 H <sub>2</sub> O	6.32 H <sub>2</sub> O

The above analysis shows the complex to be

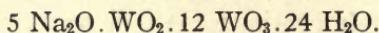


The analysis of the sodium derivative is given in Table V.

TABLE V.

Wt. of Complex.	Wt. of Constituent Found.	%	Theoretical % calculated for 5 Na <sub>2</sub> O.WO <sub>2</sub> .12 WO <sub>3</sub> .24 H <sub>2</sub> O.
0.2293 gr.	0.0135 gr. WO <sub>2</sub>	5.89 WO <sub>2</sub>	5.77 WO <sub>2</sub>
0.5062 "	0.0287 gr. "	5.67 "	
0.2646 "	0.1969 " WO <sub>3</sub>	74.41 WO <sub>3</sub>	74.40 WO <sub>3</sub>
0.2035 "	0.1508 " "	74.10 "	
0.2646 "	0.0508 " Na <sub>2</sub> SO <sub>4</sub>	8.39 Na <sub>2</sub> O	8.29 Na <sub>2</sub> O
0.2035 "	0.0382 " "	8.21 "	
	by difference	11.67 H <sub>2</sub> O	11.54 H <sub>2</sub> O

The complex, therefore, is



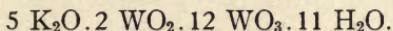
II. In an attempt to repeat the preparation of the potassium complex, the ammonium para tungstate solution was boiled up with the hydrated tungsten dioxide for a much longer time than in the first preparation. Potassium iodide, added to the solution, gave a deep brown precipitate, instead of the buff colored precipitate obtained previously. On recrystallizing from water, the difficultly soluble light brown complex, obtained before, crystallized out first. This was followed by dark brown

crystals. The latter were much more soluble in water and could easily be separated from the light brown crystals by several recrystallizations. The mother liquor from the first preparation of the light brown compound was deep brown in color and probably contained this new body. The dark brown crystals were analyzed as outlined before.

TABLE VI.

Wt. of Complex.	Wt. of Constituent Found.	%	Theoretical % calculated for 5 K <sub>2</sub> O.2 WO <sub>2</sub> .12 WO <sub>3</sub> .11 H <sub>2</sub> O.
0.8765 gr.	0.0995 gr. WO <sub>2</sub>	11.35 WO <sub>2</sub>	11.12 WO <sub>2</sub>
0.4966 "	0.0552 " "	11.12 "	
0.2111 "	0.1514 " WO <sub>3</sub>	71.72 WO <sub>3</sub>	71.68 WO <sub>3</sub>
0.5199 "	0.3716 " "	71.48 "	
0.2111 "	0.0471 " K <sub>2</sub> SO <sub>4</sub>	12.03 K <sub>2</sub> O	12.10 K <sub>2</sub> O
0.5199 "	0.1164 " "	12.09 "	
	by difference	5.11 H <sub>2</sub> O	5.10 H <sub>2</sub> O

The formula of the dark brown crystals as deduced from the above analysis, therefore, is



Lead acetate added to a solution of the potassium salt gave a heavy white precipitate. Mercurous nitrate gave a green precipitate. The ferric salt was yellow. Silver nitrate gave a chocolate colored precipitate. On boiling, the latter darkened. This was soluble in ammonium hydroxide leaving metallic silver. The cobalt salt was pink. Copper sulphate gave a greenish white precipitate.

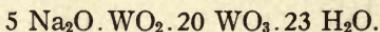
III. Sodium metatungstate, Na<sub>2</sub>O.4 WO<sub>3</sub>.10 H<sub>2</sub>O, was dissolved in water. To this solution hydrated tungsten dioxide was added and the solution was boiled for some time. The excess tungsten dioxide was filtered from the deep blue solution. On standing the solution turned green and then orange colored. The compound would not crystallize out, on concentrating and cooling the solution. It was isolated by adding alcohol, when it settled as a brown oil. The latter was separated and warmed gently in hydrogen to dry it. It soon solidified as a white crystal-

line solid. It was soluble in water giving an orange colored solution. The analysis of the sodium compound follows:

TABLE VII.

Wt. of Complex.	Wt. of Constituent Found.	%	Theoretical % calculated for 5 Na <sub>2</sub> O. WO <sub>2</sub> . 20 WO <sub>3</sub> . 23 H <sub>2</sub> O.
0.3654 gr.	0.0141 gr. WO <sub>2</sub>	3.86 WO <sub>2</sub>	3.85 WO <sub>2</sub>
0.3087 "	0.0122 " "	3.95 "	
0.7645 "	0.0286 " "	3.74 "	
0.2760 "	0.2297 " WO <sub>3</sub>	83.22 WO <sub>3</sub>	83.15 WO <sub>3</sub>
0.2472 "	0.2052 " "	83.01 "	
0.4334 "	0.3615 " "	83.41 "	
0.2760 "	0.0357 " Na <sub>2</sub> SO <sub>4</sub>	5.65 Na <sub>2</sub> O	5.55 Na <sub>2</sub> O
0.2472 "	0.0321 " "	5.67 "	
0.4334 "	0.0543 " "	5.47 "	
	by difference	7.38 H <sub>2</sub> O	7.45 H <sub>2</sub> O

The analysis indicates the formula to be



Lead acetate formed a heavy white precipitate. Mercurous nitrate gave a yellow-white precipitate, while that formed by silver nitrate was purple colored, insoluble in hot or cold water. Ferric chloride gave an orange colored precipitate. Potassium iodide added to a cooled solution of the sodium salt, gave the less soluble potassium salt of the complex in long colorless crystals.

IV. Pechard<sup>1</sup> has shown that when sulphur dioxide is passed into a solution of ordinary ammonium molybdate, compounds are formed which conform to the formula,  $4(\text{NH}_4)_2\text{O} \cdot 3 \text{ SO}_2 \cdot 10 \text{ MoO}_3 \cdot 6 \text{ H}_2\text{O}$ . It was thought that corresponding tungsten complexes might exist. Accordingly ammonium paratungstate was dissolved in water and sulphur dioxide was passed in. The gas was rapidly absorbed. The solution was concentrated by evaporating on the water bath, sulphur dioxide being passed through the solution, during the evaporation, to keep it saturated with the gas. On cooling in ice water, large colorless octahedrons formed. Some of the crystals were fully three-quarters of an inch across. They were extremely soluble in water. The com-

<sup>1</sup> Compte Rendus 116, 1441 (1893).

pound was recrystallized several times from water. Analysis showed no sulphur dioxide to be present in the compound. It proved to be ammonium metatungstate,  $(\text{NH}_4)_2\text{O} \cdot 4 \text{WO}_3 \cdot 8 \text{H}_2\text{O}$ .

TABLE VIII.

Wt. of Compound.	Wt. of Constituent Found.	%	Theoretical % calculated for $(\text{NH}_4)_2\text{O} \cdot 4 \text{WO}_3 \cdot 8 \text{H}_2\text{O}$ .
0.3014 gr.	0.0166 gr. $(\text{NH}_4)_2\text{O}$	5.52 $(\text{NH}_4)_2\text{O}$	4.63 $(\text{NH}_4)_2\text{O}$
0.5752 "	0.0315 " "	5.47 "	"
0.3424 "	0.2858 " $\text{WO}_3$	83.47 $\text{WO}_3$	82.56 $\text{WO}_3$
0.4598 "	0.3836 " "	83.43 "	"
	by difference	11.15 $\text{H}_2\text{O}$	12.81 $\text{H}_2\text{O}$

This reaction constitutes a rather quick and easy method for the preparation of ammonium metatungstate.

V. Titanium hydroxide, made by adding redistilled ammonium hydroxide to a solution of potassium titanium fluoride, and zirconium hydroxide, made by adding ammonium hydroxide to a solution of zirconium sulphate, were boiled up separately with a solution of potassium paratungstate for several hours. The excess titanium and zirconium hydroxides were filtered out in each case and the complexes were crystallized. They were analyzed by precipitating titanium and zirconium hydroxides with ammonium hydroxide and weighing them as dioxides. The tungsten trioxide and potassium sulphate were formed as outlined before.

TABLE IX.

Wt. of Complex.	Wt. of Constituent Found.	%	Theoretical % calculated for $22 \text{K}_2\text{O} \cdot \text{TiO}_2 \cdot 57 \text{WO}_3 \cdot 39 \text{H}_2\text{O}$ .
0.3746 gr.	0.0019 gr. $\text{TiO}_2$	0.51 $\text{TiO}_2$	0.50 $\text{TiO}_2$
0.4282 "	0.0021 " "	0.49 "	"
0.3746 "	0.3072 " $\text{WO}_3$	82.01 $\text{WO}_3$	82.27 $\text{WO}_3$
0.4282 "	0.3524 " "	82.30 "	"
0.3746 "	0.0901 " $\text{K}_2\text{SO}_4$	13.00 $\text{K}_2\text{O}$	12.87 $\text{K}_2\text{O}$
0.4282 "	0.1016 " "	12.82 "	"
	by difference	4.43 $\text{H}_2\text{O}$	4.36 $\text{H}_2\text{O}$

$22 \text{K}_2\text{O} \cdot \text{TiO}_2 \cdot 57 \text{WO}_3 \cdot 39 \text{H}_2\text{O}$ .

TABLE X.

Wt. of Complex.	Wt. of Constituent Found.	%	Theoretical % calculated for 29 K <sub>2</sub> O · ZrO <sub>2</sub> · 70 WO <sub>3</sub> · 73 H <sub>2</sub> O.
0.3446 gr.	0.0019 gr. ZrO <sub>2</sub>	0.55 ZrO <sub>2</sub>	0.60 ZrO <sub>2</sub>
0.3767 "	0.0024 " "	0.64 "	
0.3446 "	0.2743 " WO <sub>3</sub>	79.60 WO <sub>3</sub>	79.60 WO <sub>3</sub>
0.3767 "	0.2982 " "	79.17 "	
0.3446 "	0.0834 " K <sub>2</sub> SO <sub>4</sub>	13.09 K <sub>2</sub> O	13.36 K <sub>2</sub> O
0.3767 "	0.0975 " "	13.99 "	
	by difference	6.48 H <sub>2</sub> O	6.44 H <sub>2</sub> O

29 K<sub>2</sub>O · ZrO<sub>2</sub> · 70 WO<sub>3</sub> · 73 H<sub>2</sub>O.

Had the zirconium dioxide content been only 0.13% higher, then the formula of the zirconium dioxide complex would have corresponded exactly to the formula of the titanium dioxide complex. Both the ZrO<sub>2</sub> and the TiO<sub>2</sub> complexes were white crystalline solids, soluble in hot water.

VI. A solution of potassium paratungstate was boiled up with freshly precipitated lead dioxide. After filtering out the excess of lead dioxide, the complex was crystallized. It is a crystalline solid with a faint orange tint, soluble in water. The compound was analyzed by adding to the solution of a weighed portion, a few drops of alcohol and concentrated nitric acid. This converted the lead dioxide to lead nitrate. The solution was evaporated to dryness, the residue was baked and taken up in 1 : 1 nitric acid. The evaporation and baking were repeated twice. Nitric acid was added, then hot water containing nitric acid. The tungsten trioxide was filtered out and weighed. The filtrate containing lead nitrate and potassium nitrate was evaporated to fumes with sulphuric acid. Water and alcohol were added. The lead sulphate was filtered out and weighed. The filtrate was evaporated to dryness and the potassium sulphate was weighed.

TABLE XI.

Wt. of Complex.	Wt. of Constituent Found.	Theoretical % calculated for 64 K <sub>2</sub> O. PbO <sub>2</sub> . 171 WO <sub>3</sub> . 119 H <sub>2</sub> O.		
		%	64 K <sub>2</sub> O. PbO <sub>2</sub> . 171 WO <sub>3</sub> . 119 H <sub>2</sub> O.	
0.3341 gr.	0.0022 gr. PbSO <sub>4</sub>	0.51 Pb O <sub>2</sub>	0.50 PbO <sub>2</sub>	
0.3294 "	0.0020 " "	0.49 "		
0.3341 "	0.2763 " WO <sub>3</sub>	82.70 WO <sub>3</sub>	82.53 WO <sub>3</sub>	
0.3294 "	0.2712 " "	82.33 "		
0.3341 "	0.0772 " K <sub>2</sub> SO <sub>4</sub>	12.51 K <sub>2</sub> O	12.52 K <sub>2</sub> O	
0.3294 "	0.0767 " "	12.57 "		
	by difference	4.44 H <sub>2</sub> O	4.45 H <sub>2</sub> O	

64 K<sub>2</sub>O. PbO<sub>2</sub>. 171 WO<sub>3</sub>. 119 H<sub>2</sub>O.

It will be noticed that this formula is just three times the formula of the titanium dioxide complex.

## SUMMARY.

1. The existence of tungsten hexabromide is confirmed. Exact details are given for its preparation in larger quantities.

2. Platinum black will catalyze the reaction between chlorine and molybdenum and between bromine and molybdenum so that the formation of molybdenum pentachloride and molybdenum tetrabromide is facilitated.

3. The formulæ of the following complexes were derived from their analyses:

5 K<sub>2</sub>O. WO<sub>2</sub>. 12 WO<sub>3</sub>. 13 H<sub>2</sub>O      } analogous to 5K<sub>2</sub>O. MoO<sub>2</sub>. 12 WO<sub>3</sub>. 16 H<sub>2</sub>O  
 5 Na<sub>2</sub>O. WO<sub>2</sub>. 12 WO<sub>3</sub>. 24 H<sub>2</sub>O      } obtained by Wolcott Gibbs.  
 5 K<sub>2</sub>O. 2 WO<sub>2</sub>. 12 WO<sub>3</sub>. 11 H<sub>2</sub>O  
 5 Na<sub>2</sub>O. WO<sub>2</sub>. 20 WO<sub>3</sub>. 23 H<sub>2</sub>O

4. The following ratios were also obtained:

22 K<sub>2</sub>O. TiO<sub>2</sub>. 57 WO<sub>3</sub>. 39 H<sub>2</sub>O  
 29 K<sub>2</sub>O. ZrO<sub>2</sub>. 70 WO<sub>3</sub>. 73 H<sub>2</sub>O  
 64 K<sub>2</sub>O. PbO<sub>2</sub>. 171 WO<sub>3</sub>. 119 H<sub>2</sub>O

5. Sulphur dioxide acts upon ammonium paratungstate removing part of the volatile alkali and forming ammonium metatungstate. This forms a convenient method for the preparation of the latter compound.





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